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⑯ Electrodes having mixed metal oxide catalyst coatings and methods for producing such electrodes.

⑯ A mixed metal oxide electrocatalyst comprising oxides of at least two metals is formed by the thermal decomposition of metal-organic compounds, together with a method of producing electrodes for electrolytic processes carrying a coating of such an electrocatalyst and the electrodes themselves. The electrodes may be used either as anodes or cathodes in electrolytic processes, such as the electrolysis of alkali metal halides, electro-organic syntheses, electrowinning and water electrolysis, in electrolytic apparatus, such as fuel cells and metal/air batteries, and as insoluble anodes in plating processes.

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1 ELECTRODES HAVING MIXED METAL OXIDE CATALYST COATINGS AND METHODS  
FOR PRODUCING SUCH ELECTRODES

FIELD OF THE INVENTION

This invention relates to the art of electrode catalyst  
5 coatings and, more specifically, to mixed metal oxide coatings  
on anodes and cathodes to be used for electrolytic processes,  
such as the electrolysis of alkali metal halide solutions, water  
electrolysis, electrowinning, the operation of fuel cells,  
electro-organic syntheses and the like.

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BACKGROUND OF THE INVENTION

Electrolytic processes are utilized in the manufacture of  
many essential basic chemicals required in industrial societies.  
Among these are chlorine and caustic soda (sodium hydroxide).  
These basic chemicals are generally produced in electrolysis cells  
15 having anodes and cathodes and a brine solution electrolyte.  
Various cell designs have been utilized, including originally  
flowing mercury cathode-type cells and, more recently, diaphragm-  
type electrolytic cells and cells having cation-exchange membranes.

Originally, graphite was used as an anode both in mercury  
20 cells and in diaphragm cells. With the introduction of dimensionally-stable anodes, it became common practice to utilize  
anodes having a valve metal substrate with an electroconductive  
catalytic coating, usually containing precious metals or oxides  
thereof, in place of the graphite formerly used. Because of the  
25 ever-increasing and high cost of precious metals, the cost of  
operating such cells is high, both in terms of original conversion

- 1 to the incorporation of dimensionally-stable anodes and recoating of the anodes once the coating has deteriorated through use.

Throughout the history of diaphragm and membrane-type cells, it has been common to utilize mild steel mesh as a cathode material, 5 since other cathode materials are either cost-prohibitive or not yet fully commercialized. In recent years, interest in oxygen or air depolarized electrodes has been increasing substantially, because gas-depolarized electrodes and processes using them are highly energy-efficient. Development is under way in order to utilize, 10 such electrodes in the chlor-alkali industry. Such gas-depolarized electrodes are generally constructed of a hydrophobic polymer material, such as polytetrafluoroethylene (PTFE), along with an electroconductive material, such as carbon black or precious metal blacks on a porous substrate. Again, as with dimensionally- 15 stable anodes, an electrocatalyst generally comprising precious metals or oxides thereof is utilized to effect the reduction of oxygen gas at the electrode-gas-electrolyte interface.

Only the dimensionally-stable anode has found commercial utility in industrial electrolytic processes, because the reduction 20 in production costs offsets the substantial investment in precious metal catalysts employed therewith. A less expensive but comparably effective electrocatalyst would be of extreme value in the industry.

It is known in the art of catalysis to employ a nickel/cobalt oxide spinel form of catalyst. Thus, GB-PS 1,461,764 25 describes the preparation of nickel oxide/cobalt oxide spinel catalysts by coprecipitating the metal ions upon a substrate from the corresponding oxalates or by freeze-drying the metal nitrates in solution with liquid nitrogen and depositing them on the electrode substrate, prior to thermal decomposition. These processes 30 are very complex and require the use of highly-sophisticated equipment not necessitated by the present invention. Also, thermal decomposition of nitrates creates hazardous oxides of nitrogen, which must be disposed of.

It is also known in the art to produce an electroconductive 35 layer utilizing organometallic compounds. Thus GB-PS 1,416,072,

- 1 describes the production of transparent electrodes, whereby organometallic compounds are spray-coated on to glass or other transparent substrates and heated to a high temperature (500° to 700°C) to produce a thin transparent layer of electroconductive
- 5 metal oxide glass on the substrate surface. Such electrodes are utilized in electroluminescent flat display devices.

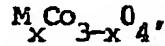
US-PS 3,528,857 discloses the use of a spinel-form catalyst of the formula  $\text{NiCo}_2\text{O}_4$  for fuel cell electrodes. The catalytic spinel is formed by dissolving inorganic salts of nickel and cobalt in a suitable solvent and then converting them to the hydroxides and drying, prior to heating in air to produce the spinel-form oxide. The resultant material may then be compressed to give a porous electrode structure. Alternatively, a solution of nickel and cobalt inorganic salts may be applied by immersing an electrode structure in the solution, followed by drying and heating to convert the nickel and cobalt salts to the spinel-form oxide.

US-PS 3,663,280 describes the use of an organo-metallic compound of a film-forming metal, such as titanium, zirconium, niobium, tantalum or tungsten, to produce a film-forming metal oxide coating on the surface of film-forming metal anodes having a precious metal catalyst applied thereto. Preferred organo-metallic compounds are the alkoxides or alkoxy-halides of film-forming metals, such as titanates or chlorotitanates. The coating serves as an inhibitor to anode base metal corrosion in the environment of an electrochemical cell.

US-PS 3,977,958 describes the use of a single metal spinel of cobalt oxide as an anode coating for chlor-alkali electrolysis. The cobalt salt of a long chain fatty acid is applied to the surface of a titanium anode substrate and heated to decompose the salt to produce the desired cobalt oxide spinel structure. The coating optionally includes "modifier oxides," which are oxides of metals selected from Groups III-B to VII-B and Groups III-A to V-A of the Periodic Table, and the lanthanides and actinides.

35 A similar modifier oxide may be used, according to US-PS

1 4,061,549, with a bimetallic oxide spinel structure of the formula



where  $x$  is greater than 0 and less than or equal to 1 and where  $M$  is a metal selected from Groups I-B, II-A or II-B of the Periodic

5 Table. The mixed metal spinel structure is obtained by applying mixed inorganic salts of cobalt and the selected metal in a volatile carrier to the surface of an anode structure.

While spinel-form oxide structures have been successfully produced upon electrode surfaces directly from solutions of metal 10 compounds, perovskite phases require the preparation of the oxide in solid powder form, followed by affixing the powder to an electrode substrate with a binder. See US-PS 3,917,525, 4,010,091 and 4,042,483.

It has now been discovered that electrocatalytic coatings 15 for electrodes can be made, using nonprecious metal oxides and this results in a substantial lowering of the cost of such coated electrodes. The invention thus provides improved electrodes made by a method, wherein the surface of an electrode substrate, selected from electrically-conductive metals and metals having an 20 electrically-conductive coating thereon, is first prepared and is then provided with a coating of an electrocatalytic mixture of metal oxides.

#### SUMMARY OF THE INVENTION

In accordance with one aspect of the invention, the electrically-conductive coating is prepared by applying to the surface 25 of the electrode substrate a mixture of at least two metal-organic compounds, such mixture comprising an organic compound of at least one first metal selected from iron, nickel, manganese, yttrium, lanthanum, the rare earth metals, thallium, lead, bismuth and 30 metals selected from Groups IA, IIA, IB and IIB of the Periodic Table, and an organic compound of at least one second metal different from the first metal or metals and selected from manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, rhodium, iridium, 35 palladium, platinum, aluminium, thallium, lead and bismuth, and heating the coated electrode substrate in an oxidizing atmosphere to an elevated temperature sufficient to convert the mixture of at least two metal-organic compounds into a mixed metal oxide electrocatalyst coating.

By operating in accordance with the invention, the two or more

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1 selected metal-organic compounds described are oxidized on the surface of the electrode to produce mixed metal oxides in spinel, bronze or perovskite form, which lower the voltage required for the electrode reaction in electrolytic processes and/or offer greatly increased lifetimes in strong electrolytes.

5 Further in accordance with the invention, the above-described at least two metal organic compounds are applied to an electrically conductive substrate. As used in this specification, the term "substrate" will be understood to include electrically conductive metals and alloys thereof as well as electrically conductive coatings of metals and metal oxides which completely 10 coat the surface of the electrode and act as a supporting substrate for the metal organic compounds used in accordance with the invention. Thus, the substrates will be understood to include iron, nickel, cobalt, copper, titanium, vanadium, zirconium, niobium, molybdenum, tantalum, tungsten, platinum, silver, gold, palladium, lead, alloys of any of these metals, and coatings on such metals of tin 15 oxide and antimony oxide, tin oxide and indium oxide, tin oxide and bismuth oxide, lead dioxide, and the precious metals and oxides thereof.

Further in accordance with the invention, an anode substrate selected from a group consisting of titanium, tantalum, zirconium, niobium or other valve metal or alloy thereof is coated with a mixture of metal organic compounds 20 which is then dried and cured at elevated temperatures to oxidize the metal components to their oxide form and create a mixed metal oxide structure on the surface of the anode substrate. The anode may then be used in electrolytic processes such as the electrolysis of water, sodium chloride, electroorganic synthesis and the like.

25 Further in accordance with the invention, a cathode substrate selected from a group consisting of iron, nickel, cobalt, alloys thereof, and air/oxygen cathode substrates such as porous graphite or porous metal or carbon black/PTFE substrates is coated with a mixture of at least two metal organic compounds of the type described. The coated cathodes are then dried and cured 30 at an elevated temperature to oxidize the metal components of the coating to their oxide form and to create a mixed metal oxide structure on the surface of the cathode substrate. The cathode may be applied to use in electrolytic processes, such as the electrolysis of sodium chloride, to make chlorine and caustic or as an oxygen reduction electrode in a fuel cell or the electrolysis 35 device.

Still further in accordance with the invention, a coating of mixed metal oxides may be deposited on electrode substrates using metal organic compounds of the type described, applying same by painting, spraying, dipping or vapor depositing on the substrate.

DETAILED DESCRIPTION OF THE INVENTION  
AND PREFERRED EMBODIMENTS

The invention will now be more clearly described in the more limited aspects of preferred embodiments thereof. It will be understood by those skilled in the art that deviations from the exemplary embodiments are possible and that it is intended that the scope of the invention not be limited to only those specific embodiments set forth hereinafter.

- 5        In accordance with the invention, a mixture of at least two metal organic compounds is applied to the surface of an electrode substrate. The organometallic compounds generally comprise metal complexes or salts of organic acids. The above-described at least two metal organic compounds comprise organic compounds of a first metal selected from a group consisting of
- 10      manganese, iron, nickel, yttrium, lanthanum, the rare earth metals, thallium, lead, bismuth and metals from periodic groups IA, IIA, IB and IIB, and at least one additional metal which differs from such first metal selected from a group consisting of manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, rhodium, iridium, palladium, platinum, aluminum, thallium, lead, and bismuth. The metal organic compounds of the selected metals are then heated on the surface of the electrode substrate to form a mixed metal oxide coating on the surface of the electrode.

Electrode substrates used in the invention are generally electrically conductive metals or electrically conductive coatings on basis metals. Thus, depending on the type of application desired for the resultant electrode, the substrate may comprise iron, nickel, cobalt, copper, gold, silver, platinum, iridium, rhenium, palladium, titanium, vanadium, zirconium, niobium, tantalum, lead, alloys of these metals and any of these metals having a coating thereon of tin oxide and antimony oxide, tin oxide and indium oxide, tin oxide and bismuth oxide, lead dioxide, or precious metals and/or their oxides. The substrate may take the form of a solid sheet, perforated plate, expanded metal mesh, wire screen, porous solid or any similar structure.

- 20
- 25

The electrode substrate may be coated by painting, spraying, immersion or other coating process using a solution of the selected metal organic compounds in a carrier such as an organic solvent such as ethanol or the like. The coated substrate is then heated to evaporate the carrier solution and to oxidize the metallic components and create the desired spinel or perovskite oxide structure.

- 30

In accordance with the invention, an electrode substrate is selected and prepared for use by cleaning. When an anode is selected as the electrode to be coated, the substrate material may be any of the various anode substrate metals common in the art but, preferably, are valve metals, such as titanium, 5 tantalum, niobium, vanadium or zirconium. The anode substrate material is cleaned and, preferably, etched in any cleaning solvent which will give a properly prepared surface, such as immersion in boiling acid solutions. The substrate may also be a valve metal base having a thin coating of precious metals or oxides thereof applied thereto with cleaning procedures modified accordingly.

10 The metal organic compounds utilized in the present invention may be metal salts of organic acids. Various compositions of such metal organic compounds are available commercially from Mooney Chemicals of Cleveland, Ohio, such as 10 percent Nickel HEX-CEM, which is a nickel salt of 2-ethylhexanoic acid; 12 percent Cobalt HEX-CEM, which is, likewise, a cobalt salt 15 of 2-ethylhexanoic acid; and 6 percent Manganese TEN-CEM, which is a manganese salt of neodecanoic acid. Optionally, the desired metal organic compounds may be prepared by normal laboratory methods known to those skilled in the art. On a smooth substrate, such as a valve metal anode, the metal organic compound may be applied by any method, but the preferred method is by 20 spraying or painting the material onto the electrode. In practice, several layers of coating may be required to build up sufficient thickness of material for effective catalytic activity and coating lifetime in electrolytic processes. The material is heated for a short period of time between each successive coating to dry same prior to the application of the next coat.

25 In one preferred embodiment utilizing a valve metal anode substrate, an initial coating of antimony doped tin oxide as substrate is applied to the metal prior to the application of the metal organic compounds. While this procedure is not necessary to the feasibility of the coating, it does offer an improved surface for the organometallic and results in a smoother, more lustrous appearance in the 30 final electrode surface. Without the use of the antimony doped tin oxide coating, the surface has a grainy, matte appearance. Further, the coating has been found to be denser and more adherent and, thus, more durable when the antimony doped tin oxide substrate is utilized.

Following the application of the metal organic compounds, the coated 35 electrode is heated to about 250°C for at least 15 minutes. The heating temperature may range from 200°C to 800°C and may last for a period of 15 to 60 minutes.

The coating in accordance with the invention may also be applied to electrodes to be used as cathodes in electrolytic processes and, for smooth substrates such as steel or nickel cathodes, with a procedure identical to that applied to anode substrates being utilized. If the electrode substrate is of a 5 porous nature, such as sintered porous nickel, porous graphite or a porous oxygen electrode substrate, such as a mixture of carbon black and Teflon, the coating method may be modified in that the porous substrate is immersed in a solution of metal organic coating material, so that the metal organic compounds soak into the porous structure of the electrode. Thus, only one immersion rather than a 10 multiplicity of coatings is necessary. Treatment of the coating to produce the mixed metallic oxide is otherwise the same.

Another and more preferred method employed where an oxygen electrode is comprised of particulate or powdered carbon and a binder component such as Teflon is to mix the metal organic compounds with the carbon and heat 15 to form the oxide prior to mixing with the binder and pressing and/or sintering into the final electrode form. Other methods of coating, such as painting or spraying, may be used. Further, since the coating is internal on a porous substrate, the antimony-doped tin oxide coating step is not utilized.

The above procedures utilizing a mixture of at least two metal 20 organic compounds selected from iron, nickel, cobalt and manganese form a spinel oxide structure when baked to oxidizing temperatures in accordance with the above-outlined procedures. The addition or substitution of other metals may serve to alter the crystalline structure of the coating to a perovskite or a bronze type structure. Further, such additions and substitutions may serve to increase 25 the electrical conductivity of the catalyst, improve the chemical and electrochemical stability of the coating and/or adjust the overvoltage for the preferential discharge of certain ions in electrochemical processes. When such additional metals are utilized, the metal organic compounds are mixed with the other selected metal organics and applied in the same manner as outlined above.

30 The following examples will serve to illustrate the invention and its preferred embodiments. Such examples should not be construed as limitations on the scope of the invention nor the claims appearing hereinafter.

EXAMPLE 1

A Ti coupon was cleaned and etched in a boiling solution of 35 concentrated HCl and deionized water (50:50). Three coats of Sb doped  $\text{SnO}_2$  were applied to the coupon by brushing a solution of Sn and Sb sulphates onto the

Ti sheet followed by thermal decomposition of the sulphates. The sulphate solution was prepared by mixing 30 ml of butanol, 9.7 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (reagent analytical grade), 1.1 g of anhydrous  $\text{SbCl}_3$  and 6 ml of 98%  $\text{H}_2\text{SO}_4$ . Each layer was predried for 15 minutes at  $120^\circ\text{C}$  and then baked for 15 minutes at  $600^\circ\text{C}$  to convert the Sn and Sb sulphates to their oxides. A solution of 12 ml of 10% Ni HEX-CEM and 5 ml of 12% Co HEX-CEM was applied by brush to the substrate and the electrode heated at  $250^\circ\text{C}$  for 15 minutes. Ten such coats were applied to yield an anode with a very smooth, adherent oxide coating and a surface coverage of  $44 \text{ g/m}^2$ . X-ray diffraction analysis of the catalyst layer indicated formation of the mixed metal oxide spinel,  $\text{CoNi}_2\text{O}_4$ . Anodes prepared in this fashion are emminently suited for alkaline water electrolysis. The anode potential in 40 gpl NaOH,  $25^\circ\text{C}$ , corrected for iR solution resistance was 0.51 V vs. SCE at  $0.15 \text{ A/cm}^2$  and 0.56 V vs. SCE at  $0.45 \text{ A/cm}^2$ . Under the same operating conditions, a pure Ni anode had single electrode potential of 0.51 V vs. SCE at  $0.15 \text{ A/cm}^2$  and 0.53 V vs. SCE at  $0.45 \text{ A/cm}^2$ . The electrode was tested as an anode in 40 gpl NaOH,  $45^\circ\text{C}$ , at a current density of  $0.45 \text{ A/cm}^2$ , and had a lifetime in excess of 3000 hours before failure (defined by total cell voltage in excess of 8.0 volts).

EXAMPLE 2

20 A Ti coupon was cleaned and etched in a boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb doped  $\text{SnO}_2$  were applied to the Ti following the procedure in Example 1. A solution of 6 ml of 10% Ni HEX-CEM and 10 ml of 12% Co HEX-CEM was applied by brush to the substrate and the electrode heated at  $250^\circ\text{C}$  for 15 minutes. Ten coats were 25 applied to yield an anode with a catalyst surface coverage of  $41 \text{ g/m}^2$ . X-ray diffraction analysis of the catalyst layer indicated formation of the mixed metal oxide spinel,  $\text{NiCo}_2\text{O}_4$ . The anode potential in 40 gpl NaOH,  $25^\circ\text{C}$ , corrected for iR solution resistance, was 0.54 V vs. SCE at  $0.15 \text{ A/cm}^2$  and 0.60 V vs. SCE at  $0.45 \text{ A/cm}^2$ . The electrode was tested as an anode in 40 gpl NaOH,  $45^\circ\text{C}$ , at a 30 current density of  $0.45 \text{ A/cm}^2$ , and had a lifetime in excess of 2500 hours.

EXAMPLE 3

A Ti coupon was cleaned and etched in a boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb dop d  $\text{SnO}_2$  were applied to the Ti coupon following the procedure in Example 1. A solution of 5 ml of 6% Mn TEN-CEM (Mn salt of neodecanoic acid) and 5 ml of 12% Co HEX-CEM was applied by brush to the substrate and the electrode heated at  $250^\circ\text{C}$  for 15

minutes. Ten coats were applied to yield an anode with a surface coverage of 22 g/m<sup>2</sup>. The anode potential in 40 gpl NaOH, 25°C, corrected for iR solution resistance, was 0.56 V vs. SCE at 0.15 A/cm<sup>2</sup> and 0.62 V vs. SCE at 0.45 A/cm<sup>2</sup>. The electrode was tested as an anode in 40 gpl NaOH, 45°C, at a current density of 0.45 A/cm<sup>2</sup>, and had a lifetime of about 1700 hours.

EXAMPLE 4

A Ti mesh coupon was cleaned and etched in a boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb doped SnO<sub>2</sub> were applied to the Ti following the procedure in Example 1. A solution consisting of 10 12 ml of 10% Ni HEX-CEM and 20 ml of 12 % Co HEX-CEM was prepared. Ten coats of the mixed salt solution was applied by brush to the substrate with a 20 minute thermal treatment at 300°C following each coating application. The NiCo<sub>2</sub>O<sub>4</sub> coated electrode was installed in a cell containing 400 gpl NaOH at 85°C and was anodically polarized at a current density of 0.032 A/cm<sup>2</sup>. A stable 15 half cell potential was maintained for over 4300 hours.

EXAMPLE 5

An electrode with a NiCo<sub>2</sub>O<sub>4</sub> coating was prepared as in Example 4. The electrode was installed in a cell containing 400 gpl NaOH at 85°C and was 20 anodically polarized at a current density of 0.073 A/cm<sup>2</sup>. A stable anode half cell potential was maintained for over 2200 hours.

EXAMPLE 6

A Ti sheet coupon was cleaned and etched in a boiling aqueous solution of 18% HCl. Three coats of Sb doped SnO<sub>2</sub> were applied to the Ti following the procedure in Example 1. A layer of Pt black (~ 1.0 g/m<sup>2</sup>) was then 25 electroplated onto the electrode from a solution of 2% chloroplatinic acid in 2N HCl by polarizing the substrate cathodically with 1 amp for 5 minutes. An equimolar solution of lanthanum and cobalt octate was brushed onto the electrode and the electrode dried for 15 minutes at 120°C and then baked for 15 minutes at 600°C. A topcoat of the perovskite phase, LaCoO<sub>3</sub>, was formed by 30 this method. After applying ten layers of the LaCoO<sub>3</sub>, the resultant electrode was polarized anodically in a solution of 300 gpl NaCl, pH ~1, 75°C, at current densities of 0.15 A/cm<sup>2</sup>, 0.45 A/cm<sup>2</sup>, and 0.75 A/cm<sup>2</sup> to yield iR free single electrode potentials vs. SCE of 1.10 V, 1.16 V, and 1.20 V, respectively.

EXAMPLE 7

A Ti sheet coupon was cleaned and etched in boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb doped  $\text{SnO}_2$  were applied to the Ti following the procedure in Example 1. A solution of lanthanum octoate was prepared by dissolving 5.68 g of lanthanum octoate (ROC/RIC Chemicals) in 50 ml of toluene and 7 ml of 2-ethyl hexoic acid (Union Carbide). An equimolar solution of lanthanum and cobalt octoate was prepared by combining 1.01 g of 12% Co HEX-CEM with 10 ml of the La octoate solution. Ten coats of the mixed salt solution were then applied by brush to the electrode substrate with a 15 minute heat treatment at  $120^\circ\text{C}$  and a 15 minute heat treatment at  $600^\circ\text{C}$  following each coating application. X-ray diffraction identified the perovskite phase,  $\text{LaCoO}_3$ , to be present on the electrode surface. The single electrode potentials of this electrode when polarized anodically in a solution of 300 gpl NaCl, pH  $\approx$  1 at  $75^\circ\text{C}$  were as follows: 1.09 V ( $0.75 \text{ A/cm}^2$ ); 1.15 V ( $0.45 \text{ A/cm}^2$ ); 1.18 V ( $0.75 \text{ A/cm}^2$ ). Table 1 summarizes the polarization data for the perovskite phases.

EXAMPLE 8

A Ti sheet coupon was cleaned and etched in a boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb doped  $\text{SnO}_2$  were applied to the Ti following the procedure in Example 1. An equimolar solution of lanthanum and cobalt octoate was prepared by combining 2.01 g of 12% Co HEX-CEM and 20 ml of La octoate solution. Twelve coats of the solution were applied by brush to the electrode substrate. After each coating application, the electrode was dried at  $200^\circ\text{C}$  for 15 minutes and then baked at  $600^\circ\text{C}$  for 15 minutes. The  $\text{O}_2$  single electrode potentials in 40 gpl NaOH and 150 gpl  $\text{H}_2\text{SO}_4$  are shown in Table 1.

EXAMPLE 9

A Ti sheet coupon was cleaned and etched in a boiling solution of concentrated HCl and distilled water (50:50). Three coats of Sb doped  $\text{SnO}_2$  were applied to the Ti following the procedure in Example 1. An equimolar solution of lanthanum and manganese octoate was prepared by combining 3.75 g of 6% Mn HEX-CEM and 20 ml of La octoate solution. Twelve coats of the solution were applied by brush to the electrode substrate. After each coating application, the electrode was dried at  $200^\circ\text{C}$  for 15 minutes and then cured at  $600^\circ\text{C}$  for 15 minutes. X-ray diffraction revealed  $\text{LaMnO}_3$  as the major phase in the electrode

surface. The single electrode potentials in 40 gpl NaOH and 150 gpl  $H_2SO_4$  are shown in Table 1.

TABLE 1

Single Electrode Potentials of Example 7-9 Electrodes

		300 gpl NaCl pH ~1 75°C	150 gpl $H_2SO_4$ 50°C	40 gpl NaOH 25°C
5	Perovskite	Current Density (A/cm <sup>2</sup> )		
	LaCoO <sub>3</sub> (Ex. 7&8)	0.075 0.45	1.09 1.15	1.41 1.45
10		0.75	1.18	1.47
	LaMnO <sub>3</sub> (Ex. 9)	0.075 0.45 0.75	-- -- --	1.44 1.50 1.65
				0.55 0.61 0.64 0.73 0.84 0.91

EXAMPLE 10

15 A 1" x 3" mild steel mesh coupon was sandblasted, rinsed in water and acetone dried. A solution of 10 ml of 6% Mn TEN-CEM (Mn(II) salt of neodecanoic acid, Mooney Chemicals) and 10 ml of 12% Co HEX-CEM (Co(II) salt of 2-ethylhexanoic acid, Mooney Chemicals) was applied by brush to the steel surface and the steel coupon was baked at 250°C for 15 minutes. After allowing  
20 the coupon to cool to room temperature, a second coat of the oxide was applied in the same manner. Seven additional coats of the mixed metal salt solution were brushed onto the electrode surface followed by baking at 295°C for 15 minutes after each coating application. The electrode was polarized cathodically in a solution of 100 gpl NaOH at 90°C and showed single electrode potentials for  
25  $H_2$  evolution of 1.04, 1.08 and 1.14 volts vs SCE at current densities of 0.075, 0.15 and 0.30 A/cm<sup>2</sup>, respectively. In comparison, a plain steel mesh cathode had single electrode potentials in 100 gpl NaOH at 90°C of 1.17, 1.22, and 1.28 volts vs. SCE at current densities of 0.075, 0.15 and 0.30 A/cm<sup>2</sup>, respectively.

EXAMPLE 11

A 1" x 3" mild steel mesh coupon was sandblasted, rinsed in water and acetone dried. A solution of 6 ml of 10% Ni HEX-CEM and 10 ml of 12% Co HEX-CEM was brushed onto the steel surface and the steel coupon was baked at 250°C for 15 minutes. A second coat of the oxide was applied in the same manner. Seven additional coats of the mixed metal salt solution were brushed onto the electrode followed by baking at 295°C for 15 minutes after each coating application. The electrode was polarized cathodically in a solution of 100 gpl NaOH at 90°C and showed single electrode potentials for H<sub>2</sub> evolution of 1.08, 1.14 and 1.20 volts vs. SCE at current densities of 0.075, 0.15 and 0.30 A/cm<sup>2</sup>, respectively.

EXAMPLE 12

A 1" x 3" mild steel mesh coupon was sandblasted, rinsed in water and acetone dried. A solution of 12 ml of 10% Ni HEX-CEM and 5 ml of 12% Co HEX-CEM was brushed onto the steel surface and the steel coupon was baked at 250°C for 15 minutes. A second coat of the oxide was applied in the same manner. Seven additional coats of the mixed metal salt solution were brushed onto the electrode surface followed by baking at 295°C for 15 minutes after each application of the solution. The electrode was polarized cathodically in a solution of 100 gpl NaOH at 90°C and showed single electrode potentials for H<sub>2</sub> evolution of 1.13, 1.17 and 1.24 volts vs. SCE at current densities of 0.075, 0.15 and 0.30 A/cm<sup>2</sup>, respectively.

EXAMPLE 13

A-sintered Ni sheet (14.5 cm<sup>2</sup>) was etched in aqua regia to provide a clean surface and soaked with a solution of 1.0 g of 10% Ni HEX-CEM; 1.7 g of 12% Co HEX-CEM and 5 ml of ethanol. The sheet was then heated in a furnace at 250°C for one hour and 350°C for one hour. A cathode potential of -306 mv vs. Hg/HgO at 0.31 A/cm<sup>2</sup> was observed.

EXAMPLE 14

A cryogenically pre-mixed composite of carbon black (600 m<sup>2</sup>/g) and DuPont Teflon 30 (Liquid Nitrogen Processing Corporation) was pressed at room temperature into a sheet (14.5 cm<sup>2</sup> x 0.12 cm). The cold pressed substrate was soaked in a solution of 1.0 g of 10% Ni HEX-CEM (Ni salt of 2-ethylhexanoic acid, Mooney Chemicals), and 30 ml of ethanol and then sintered at 350°C for 10

minutes at 10,000 lbs. ram pressure. The electrode was operated as an  $O_2$  cathode in 400 gpl caustic,  $60^\circ C$ , 22 mm Hg at  $0.31 \text{ A/cm}^2$  and showed a -350 mv vs. Hg/HgO cathode potential.

EXAMPLE 15

5 Stoichiometric amounts of nickel and cobalt HEX-CEM to make carbon loaded with 30%  $NiCo_2O_4$  was added to carbon powder (Vulcan XC72R). This mixture was fired in a furnace at  $250^\circ C$  overnight to oxidize the metal organic compounds to  $NiCo_2O_4$  spinel. This material was then mixed with Teflon 10 in an alcohol and water mixture and formed into a sheet. The sheet was then air dried and pressed into a current distribution mesh (nickel) and sintered at  $350^\circ C$ . When operated as an oxygen cathode in concentrated NaOH solution, stable performance at 0.31 amps per square centimeter was noted with a potential of -0.42 volts vs. an Hg/HgO electrode.

15 While the invention has been described in the more limited aspects of preferred embodiments thereof, other embodiments have been suggested and still others will occur to those skilled in the art upon the reading and understanding of the foregoing specification. It is intended that all such embodiments be included within the scope of the appended claims and that the foregoing disclosure of preferred embodiments shall in no way limit the scope thereof.

## 1 CLAIMS:

1. A method for producing an electrode suitable for carrying out electrolytic processes, wherein the surface of an electrode substrate, selected from electrically-conductive metals and metals having an electrically-conductive coating thereon, is first prepared and is then provided with a coating of an electro-catalytic mixture of metal oxides, characterised in that the coating is prepared by:
  - 10 applying to the surface of the electrode substrate a mixture of at least two metal-organic compounds, such mixture comprising an organic compound of at least one first metal selected from iron, nickel, manganese, yttrium, lanthanum, the rare earth metals, thallium, lead, bismuth and metals selected from Groups IA, IIIA, IB and IIB of the Periodic Table, and an organic compound of at least one second metal different from the first metal or metals and selected from manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, rhodium, iridium, palladium, platinum, aluminium, thallium, lead and bismuth, and heating the coated electrode substrate in an oxidizing atmosphere to an elevated temperature sufficient to convert the mixture of at least two metal-organic compounds into a mixed metal oxide electrocatalyst coating.
  - 25 2. A method according to claim 1, wherein the mixture of metal-organic compounds is applied by being sprayed on to the electrode substrate surface.
  - 30 3. A method according to claim 1, wherein the mixture of metal-organic compounds is applied by painting at least one layer of the mixture upon the electrode substrate surface.
  4. A method according to claim 1, wherein the mixture of metal-organic compounds is applied to the substrate surface by immersing the electrode substrate in a solution of the mixture.
  - 35 5. A method according to any preceding claim, wherein the electrode substrate is a valve metal and the substrate surface

1 is prepared by cleaning and etching the substrate and then providing a coating of antimony-doped tin oxide upon the prepared substrate surface.

6. A method according to claims 1 to 4, wherein the 5 electrode substrate is a cathode substrate selected from nickel, iron, mild steel, cobalt and alloys thereof and its surface is prepared by cleaning and etching the cathode substrate.

7. A method according to any of claims 1 to 4, wherein 10 the electrode substrate comprises a porous air/oxygen electrode substrate and its surface is prepared by pressing the substrate in a cold press.

8. An electrode suitable for carrying out aqueous electrolytic processes, having a spinel-form coating thereon produced by a method according to any of claims 1 to 4.

15 9. An electrode suitable for carrying out aqueous electrolytic processes, having a coating thereon produced by a method according to any of claims 5 to 7.

10. A method of preparing a porous gas electrode, characterised in that:

20 powdered substrate material is mixed with a solution containing at least two metal-organic compounds, one being a compound of a first metal selected from iron, nickel, manganese, yttrium, lanthanum, the rare earth metals, thallium, lead, bismuth and metals selected from Groups IA, IIA, IB and IIB of the Periodic 25 Table, and the other being a compound of at least one second metal different from the first metal and selected from manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, rhenium, iridium, palladium, platinum, aluminium, thallium, lead and 30 bismuth;

the mixture of powdered substrate material and metal-organic compounds is baked at an elevated temperature in the range from 200° to 600°C for a period sufficient to convert the metal-organic compounds to a mixed metal oxide coating on the substrate 35 material;

- 1 and pressing the resultant composite product to form a porous electrode material.
11. A method according to claim 10, wherein the powdered substrate material is selected from organic monomeric
- 5 and polymeric materials, asbestos, clay, graphite and carbon black.
12. A porous gas electrode, comprising a pressed composite powder product made by a method according to claim 10 or 11.



European Patent  
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EUROPEAN SEARCH REPORT

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Application number

EP 80300392.0

DOCUMENTS CONSIDERED TO BE RELEVANT		CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	<p><u>AT - B - 316 589</u> (FIRMA C.CONRADTY) + Examples; claims + --</p> <p><u>DD - A - 131 568</u> (DIAMOND SHAMROCK TECHNOLOGIES S.A.) + Claims 1,4,5 + --</p> <p><u>GB - A - 1 195 871</u> (CHEMNOR AKTIENGESELLSCHAFT) + Pages 1,2; examples XIII, XIV; claims + --</p> <p><u>US - A - 3 689 383</u> (BERNARD J. DE WITT) + Totality + --</p> <p><u>GB - A - 1 329 855</u> (DIAMOND SHAMROCK CORPORATION) + Claim 1; page 1, lines 69-90; page 2 + --</p> <p><u>US - A - 3 773 554</u> (A. SCRUTTON) + Claims; columns 1-6 + --</p>	1,5,8, 9 1,9 1,9 1,3,5, 9 1-5,9 1,3,5,9 1,5,9
		TECHNICAL FIELDS SEARCHED (Int.Cl.3)
		C 25 B C 25 C C 25 D H 01 M C 23 C
		CATEGORY OF CITED DOCUMENTS
		<p>X: particularly relevant</p> <p>A: technological background</p> <p>O: non-written disclosure</p> <p>P: Intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
		&: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims	
Place of search	Date of completion of the search	Examiner
VIENNA	02-04-1980	HEIN